

ELECTROCHEMICAL EVALUATION OF La-Ni-Sn METAL HYDRIDE ALLOYS

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Abstract

A detailed electrochemical evaluation of Sn-modified LaNi_5 was performed to evaluate its applicability as negative electrode in alkaline rechargeable cells. Substituting small amounts of Sn for Ni provides a large improvement in the initial capacity and cyclic lifetime of the electrode, and also serves to improve the kinetics of hydrogen absorption-desorption processes.

Int reduction

The replacement of cadmium in a nickel-cadmium (Ni-Cd) cell with a metal hydride anode (Ni-MH) holds the promise of higher specific energy, higher energy density, longer cycle lifetime, and increased environmental compatibility, while retaining the capabilities of fast charge and discharge rates and facile gas recombination. The high hydrogen absorption capability, easy synthesis, and mild activation of LaNi_5 and its alloys motivated previous studies of the material in battery electrodes¹⁻³. Unfortunately, this previous work identified a rapid decline in the alloy's

hydrogen absorption capability during absorption-desorption (charge-discharge) cycling. The prevailing methodology used to slow this degradation has been to substitute small amounts of other elements for both Ni and La. Willems et al.¹ improved the alloy stability by a partial substitution of Si and Co for Ni, and of Nd for La. Sakai et al.² performed a rigorous evaluation of several elements as ternary solutes in $\text{LaNi}_{5.8}\text{M}_8$. The equilibrium hydriding pressure of the alloy was found to decrease with each of the elements Cr, Co, and Cu, and markedly so with Al and Mn. In addition, the cycle life was found to improve upon the substitution of Ni with the ternary solute in the order $\text{Mn} < \text{Ni} < \text{Cu} < \text{Cr} < \text{Al} < \text{Co}$. Another effect of the ternary substitutions for Ni, except in the case of Mn, was to increase the overpotential for the desorption reaction. In other studies, Sakai et al. showed that substituting any of Ti^3 , Zr^4 , Nd^5 , and Ce^6 for La also enhances the cycle lifetime. In all the above ternary alloys, the improvement in the cycle lifetime is unfortunately accompanied by a decrease in the hydrogen absorption capacity, long activation, or slow kinetics.

The present letter presents results from an initial evaluation of using Sn as a substituent for Ni to enhance the durability of the metal hydride. These studies were prompted by results from gas-phase thermal cycling of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ which showed as much as a 20-fold lifetime improvement over LaNi_5 ⁷.

Experimental

The $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ alloys were prepared in an arc-melting furnace and annealed in vacuum at 950°C for 72 hours. The alloys were then crushed to 10 mesh in an argon glove box, followed by several hydrogen absorption-desorption cycles to optimize the powder's surface area. The fine alloy powder ($<75\mu\text{m}$) was mixed with 19% conductive diluent, i.e. INCO nickel powder (1 μm), and 570 Teflon binder. The electrodes were fabricated by hot-pressing the mixture onto an expanded Ni screen. The electrodes for the basic electrochemical studies were fabricated by filling the BAS disk electrodes with electrode powders of equal quantities to ensure consistent

values for the electrode area (0.07 cm^2) and porosity. The Ni-MH test cells ($\sim 250 \text{ mAh}$) contained excess positive electrode (Ni(OOH)), excess electrolyte (31% KOH), and a HgO/Hg reference electrode.

Results and Discussion

Fig. 1 shows the electrochemical isotherms of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ during absorption and desorption of hydrogen. The equilibrium pressures were calculated from the equilibrium potentials using the equation⁴: $E_0 \text{ (VS. HgO/Hg)} = -0.9324 - 0.0291 \ln(P_{\text{H}_2})$. As may be seen from the isotherms, the equilibrium pressure of LaNi_5 decreases upon the addition of Sn from an initial value of $\sim 2 \text{ atm}$ to below 1 atm . This decrease in the equilibrium plateau pressure may be related to the increase in the unit cell volume⁸. X-ray diffractometry was used to characterize the material's microstructure and measure the lattice parameters of the binary and ternary alloys. Fig. 2 shows the powder diffraction pattern of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$, verifying that it is single phase. There is an increase in the unit cell volume upon the substitution of Sn accompanying the decrease in the equilibrium pressure. From the X-ray diffraction data, the unit cell volume of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ is estimated to be 89.992 \AA^3 as compared to 86.800 \AA^3 for LaNi_5 , i.e., a 3.7% increase in the unit cell Volume.

The charge-discharge behavior of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ electrodes is superior to that of LaNi_5 . $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ electrodes showed a high initial capacity of 250 mAh/g in the flooded cell and $\sim 275\text{--}300 \text{ mAh/g}$ in the prismatic cell. Under these conditions, LaNi_5 could not be completely charged, since its equilibrium pressure is higher than 1 atm . Additionally, the average charging voltage for the Sn-modified LaNi_5 is lower for than the binary material. The charge voltage fluctuated in the case of LaNi_5 owing to a significant evolution of hydrogen on the electrode surface.

The electrochemical kinetics for the hydrogen absorption and desorption process were determined by DC polarization methods. The linear and Tafel polarization curves of these alloys

are shown in figures 3a and 3b, respectively, and the results are listed in Table 1. The linear polarization curves are fairly linear enabling us to calculate the polarization resistance from their slopes. The Tafel polarization curves reveal the interference of mass transfer at high overpotentials, for which corrections have been made to the Tafel plots. The cathodic Tafel plot of LaNi_5 appears to show a different slope at high overpotentials, possibly corresponding to hydrogen evolution. The exchange current densities obtained from the linear and Tafel polarizations reveal that the absorption and desorption processes are faster in the ternary alloy than in the binary. This is not surprising, as bimetallic Sn-noble metal catalysts are known to function as electrocatalysts, e.g. in the electrochemical oxidation of methanol from aqueous solutions. The presence of a tin oxide on the electrode surface would facilitate the dissociative adsorption of a proton, which is a precursor for hydrogen absorption.

Finally, the performance of the Sn-modified alloy during charge-discharge cycling in the negative-limited, prismatic Ni-MH cells is shown in Fig. 4. The cells were charged @ 5 hour rate to 120% of charge return and η is low (below 35 mAh/g), due to the incomplete charging. In comparison, the performance of the ternary alloy is rather impressive. Apart from a high initial capacity, $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ also exhibits excellent capacity retention during charge-discharge cycling. The capacity after 100 cycles is above 50% of its initial capacity. Indeed, the capacity retention during cycling of the Sn-substituted alloy is comparable to that of the AB_5 alloys evaluated at JPI¹⁰. For example, the slope of the capacity versus cycle lifetime curve for $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ electrodes is almost identical to the best of the (Mm) $(\text{Ni-Co-Mn-Al})_5$ alloys with optimum ratios of La and Ce/Nd in the misch metal and Co, Mn and Al for the Ni sites.

Conclusions

The substitution of a small amount of Sn for Ni in LaNi_5 results in several desirable properties for the battery electrode applications, such as low equilibrium pressures, high charge efficiency, improved cycle lifetime, and fast absorption and desorption kinetics. On a volume

fraction basis, Sn appears to be the most potent substituent for improving the cyclic lifetime of LaNi₅ battery electrodes. Studies are underway to optimize the tin content in La-based as well as misch metal-based alloys.

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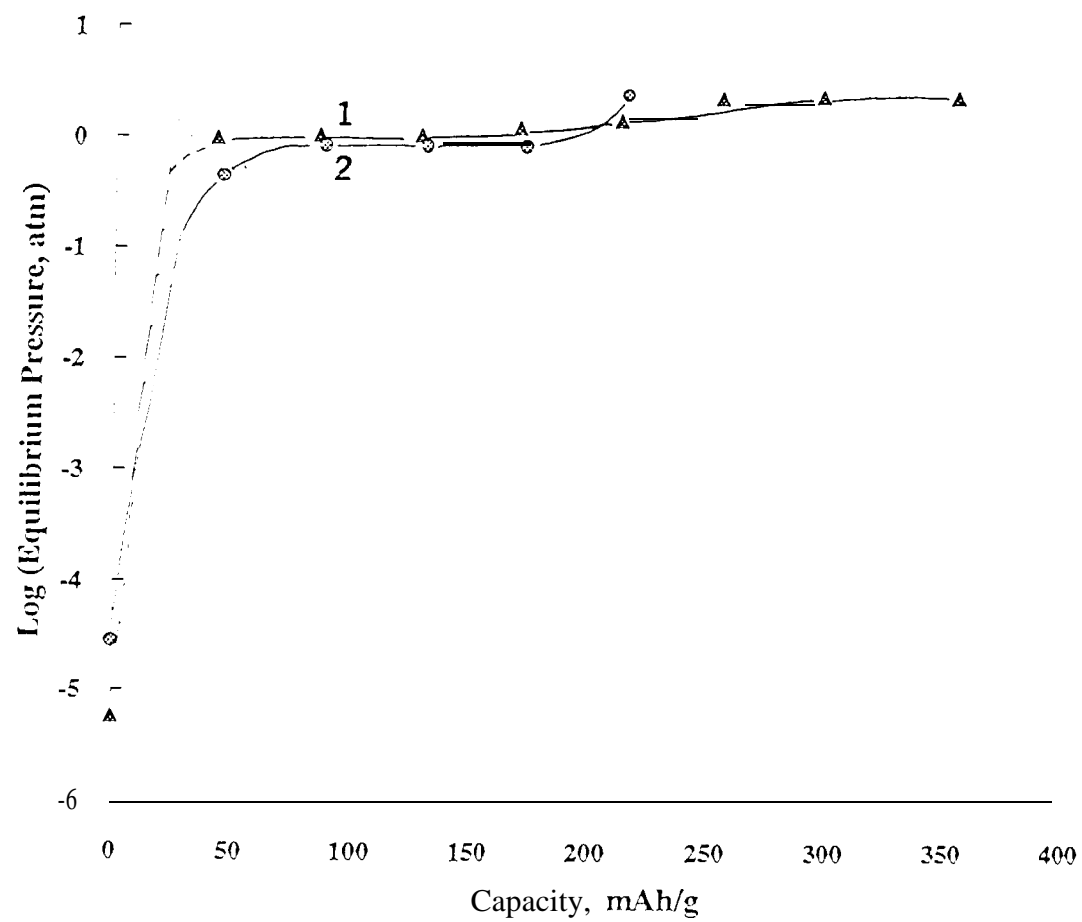
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FIGURE CAPTIONS

- Fig. 1 : Electrochemical isotherms during charge and discharge of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$
- Fig. 2 : X-ray diffraction pattern of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$
- Fig. 3 : A) Linear and B) Tafel polarization (corrected for mass transfer effects) plots of 1) LaNi_5 and 2) $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ electrodes (area : 0.07 cm^2)
- Fig. 4 : Variation of the capacity of 250 mAh, negative limited Ni-h411 cells containing 1) LaNi_5 and 2) $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ during cycling @ 5 h rate.



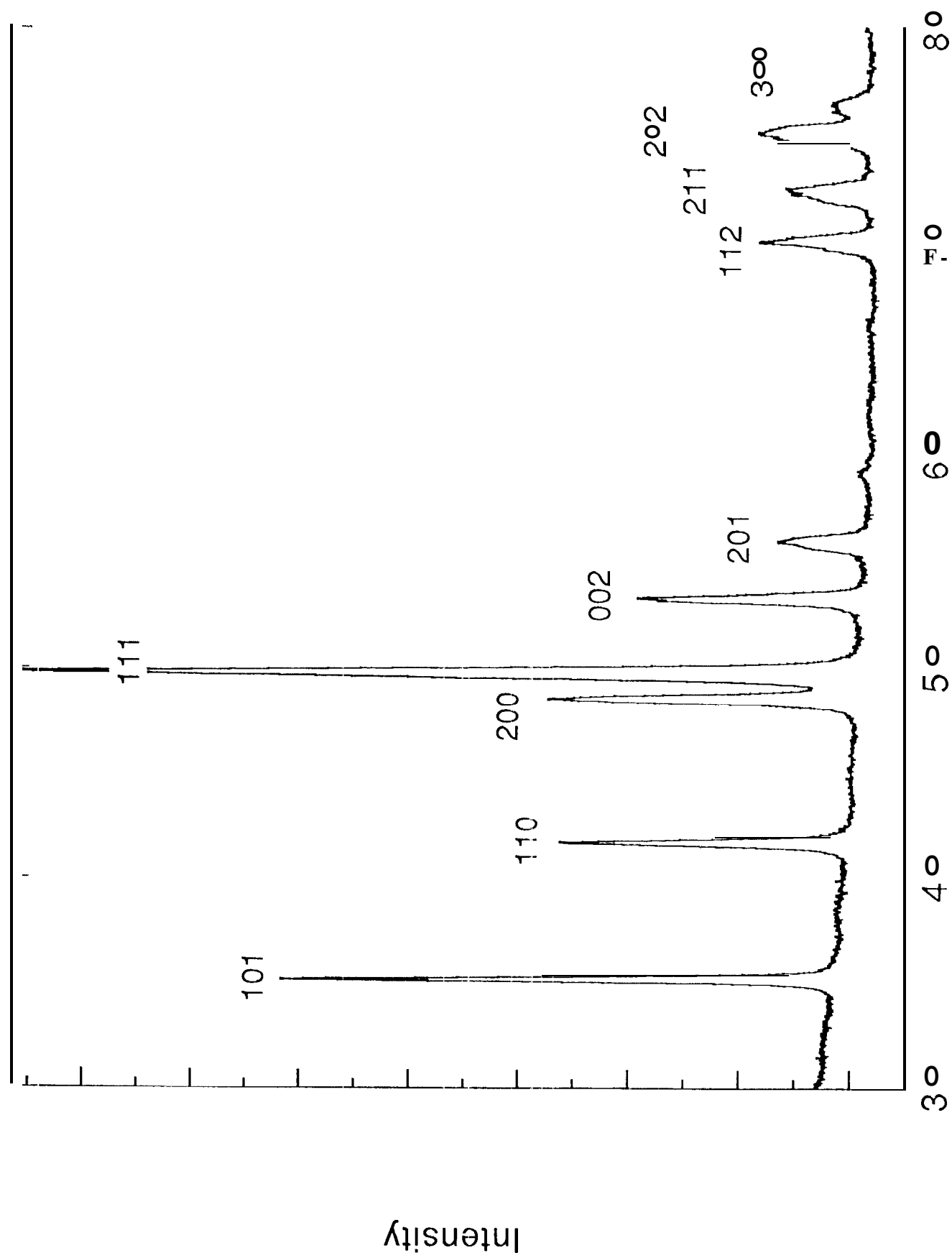


Fig 2

Two Theta (°)

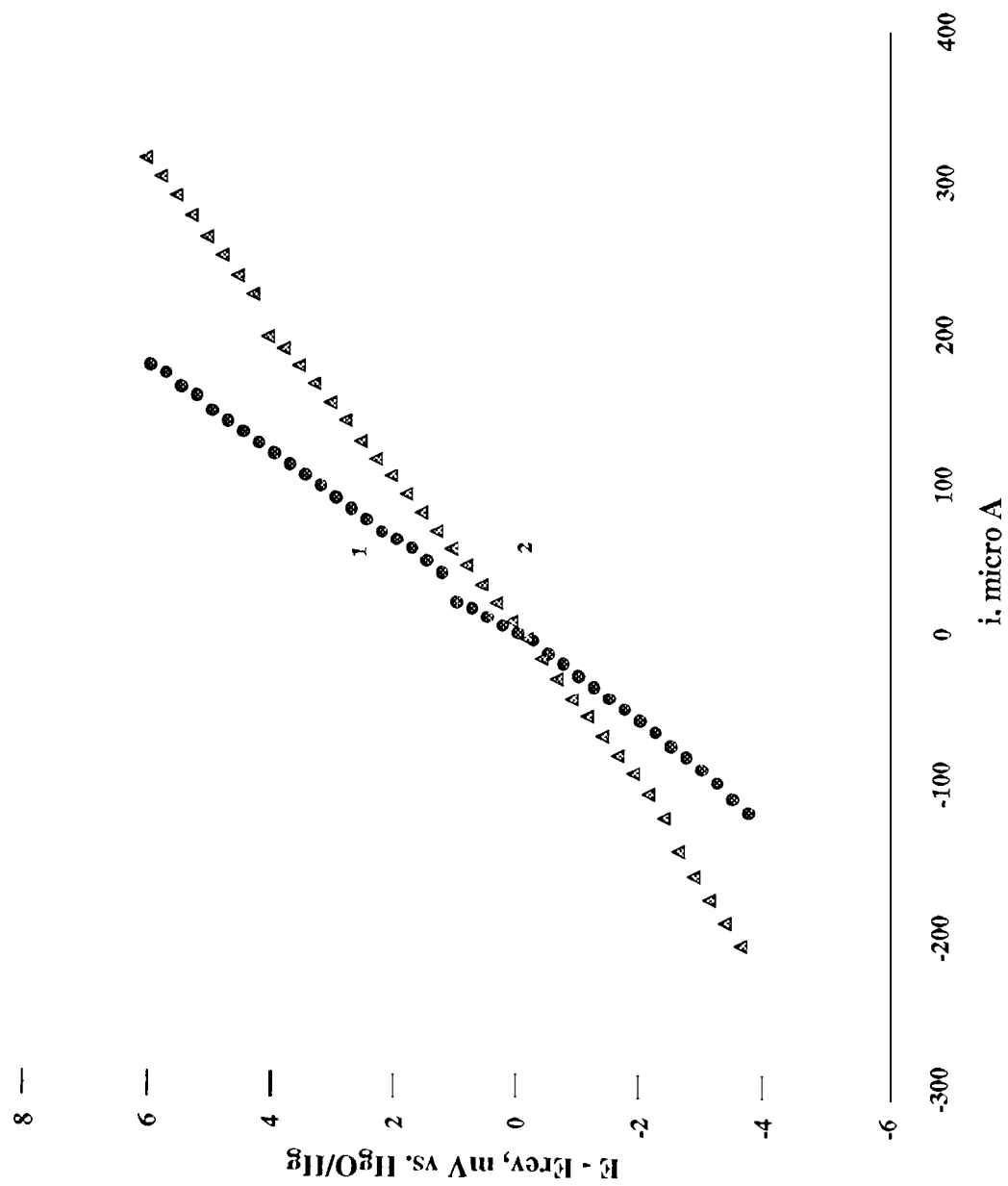
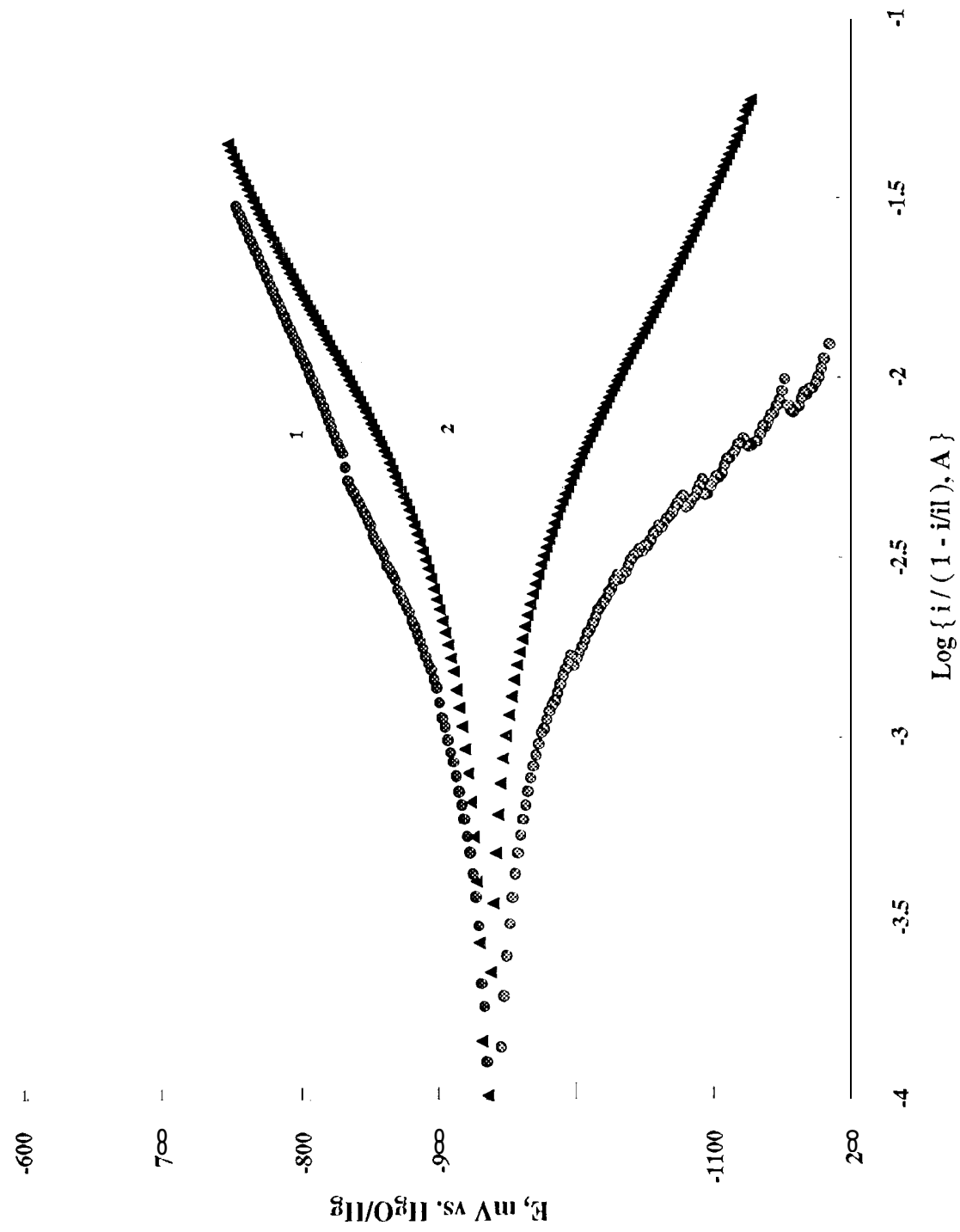


Fig 3A



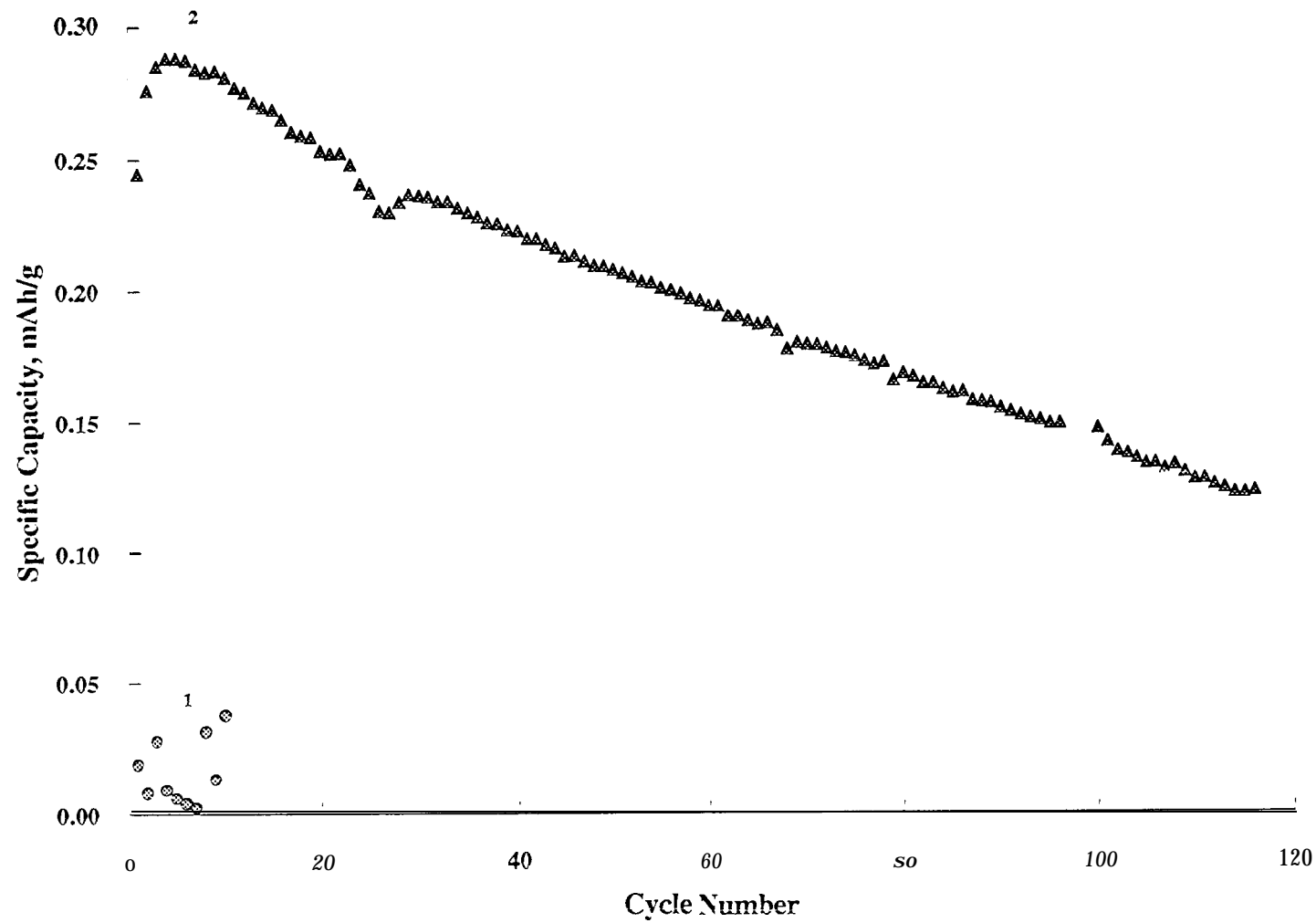


Fig-4

Table 1. Electrochemical Kinetic Parameters of LaNi_5 and $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ Anodes

	LaNi ₅		LaNi _{4.8} Sn _{0.2}	
Linear Polarization				
Polarization resistance (Ω.cm ²)	2.33		1.35	
Exchange current density (10 ⁻⁴ A.cm ⁻²)	1.1		1.9	
Tafel Polarization				
	Oxidation	Reduction	Oxidation	Reduction
Cathodic Tafel plot (mV)	129	134	242	108
Transfer coefficient	0.25	0.54	0.46	0.44
Exchange current density (10 ⁻⁴ A.cm ⁻²)	7.5	8.2	22.5	26